SYNTHESIS AND CHARACTERIZATION OF GRAPHENE FILLED EPOXY AND PEDOT:PSS COMPOSITES

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2018

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by

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Thesis submitted in fulfillment of the
requirements for the degree of
Master of Science

September 2018

ACKNOWLEDGEMENT

First of all, I would like to express my gratitude to Allah SWT for the blessing, strength and every ni'mat He bestowed upon me. Alhamdulillah, I have this research completed. Besides that, I would like to express my gratitude to my supportive supervisor, Professor Ir. Dr. Mariatti Jaafar @ Mustapha for her guidance, inspiration and supervision throughout this research project. The supervision and support that she gave truly help the progression and smoothness of this project. The cooperation and commitment from her is much indeed appreciated.

My grateful thanks also goes to all the technical staffs of School of Materials and Mineral Resources Engineering for their kind assistance, which assisted in the completion of my analysis. A big contribution and hard work from them is very great indeed especially when my project is carried out.

I also extend my acknowledgement to the Ministry of Higher Education, Malaysia for awarding MyBrain15 and Fundamental Research Grant Scheme (FRGS) for granting the research fund used for this project (Project No.6071284).

Last but not least, special thanks to my fellow friends and colleagues, for all their full support and presence, which helped me greatly throughout this research. Not to forget, my warmest appreciation to my family for their continuous encouragements emotionally and spiritually which on the whole, it would have been impossible for me to complete this research.

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LIST OF ABBREVIATIONS

AEP	Anodic electropolymerization
CNT	Carbon nanotubes
Cu	Copper
CVD	Chemical vapor deposition
DGEBA	Diglycidyl ether of bisphenol-A
FESEM	Field emission scanning electron microscope
FTIR	Fourier-transform infrared
GNS	Graphene nanosheets
GO	Graphene oxide
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulfuric acid
H_3PO_4	Phosphoric acid
HCl	Hydrogen chloride
HDPE	High-density polyethylene
HI	Hydroiodic
KClO3	Potassium chlorate
$KMnO_4$	Potassium permanganate
LLDPE	Linear low-density polyethylene
NaOH	Sodium hydroxide
$NH_2NH_2•H_2O$	Hydrazine hydrate
Ni	Nickel
PANI	Polyaniline
PDMS	Polydimenthylsiloxane

PEDOT:PSS	Poly(ethylene-3,4-dioxythiophene) : poly(styrenesulfonicacid)
PMMA	Poly(methyl methacrylate)
PS	Polystyrene
QHE	Quantum hall effect
RGO	Reduced graphene oxide
SiC	Silicon carbide
SiO_2	Silicon dioxide
T_g	Glass transition temperature
XRD	X-ray diffraction

LIST OF SYMBOLS

θ	Angle of diffraction
A/cm^2	Ampere per square centimeter
Å	Angstrom
cm	Centimeter
°C	Degree celcius
°C/min	Degree celsius per minutes
eV	Electron volt
eV/nm^2	Electron volts per newton meter square
F	Farad
F/cm^3	Farads per centimeter cube
F/g	Farads per gram
g	Gram
g/mol	Gram per mole
n	Integar number
d	Interatomic spacing
K	Kelvin
kHz	Kilohertz
MPa	Megapascal
m^2g^{-1}	Meter square per gram
μm	Micrometre
mg/ml	Miligram per milliliter
M	Molar
nF	Nanofarad

nm	Nanometre
Nn/lm^2	Nanonewton per lumen square
Ω	Ohm
Ωm	Ohm-meter
Ω/sq	Ohm per square
%	Percentage
cm^{-1}	Reciprocal centimeter
rpm	Rotation per minute
S/m	Siemens per meter
$cm^2v^{-1}s^{-1}$	Square centimeters per volt per second
TPa	Terapascal
V	Volt
Vol%	Volume percent
$Wm^{-1}K^{-1}$	Watts per meter kelvin
λ	Wavelength

SINTESIS DAN PENCIRIAN EPOKSI DAN PEDOT:PSS KOMPOSIT TERISI GRAFEN

ABSTRAK

Penemuan komposit grafen telah mendorong perubahan di kalangan para penyelidik kerana sifatnya yang unik. Tujuan kajian ini adalah untuk mensintesis grafen dan digunakan sebagai pengisi dalam komposit epoksi. Prestasi grafen yang disintesis dalam epoksi dibandingkan dengan grafen komersial. Grafen telah disintesis menggunakan kaedah Hummer yang telah diubahsuai dan salutan putaran digunakan untuk menghasilkan komposit epoksi dengan jumlah pemuatan pengisi yang berlainan. Analisis terhadap grafen yang disintesis menggunakan spectra Raman menunjukkan peningkatan nisbah keamatan (I_D/I_G) yang menyebabkan pengurangan saiz purata domain sp^2 setelah penurunan GO. Ini disebabkan oleh kehilangan pembentukan karbon. Selain itu, spectra FTIR menunjukkan bahawa grafit telah berjaya dioksidakan disebabkan kehadiran puncak yang merujuk kepada kumpulan yang mengandungi oksigen. Muatan pengisi grafen dalam epoksi yang terbaik diperoleh pada 0.4% berdasarkan pengukuran kekonduksian terma yang menunjukkan kenaikan 37.5% berbanding epoksi yang tidak terisi. Selain itu, komposit grafen/epoksi menunjukkan bahawa penambahan pengisi dalam epoksi secara amnya meningkatkan nilai kekonduksian elektrik dari 7.38×10^{-6} hingga 7.19×10^{-5} S/cm, yang merupakan dua susunan magnitud lebih tinggi daripada epoksi yang tidak terisi. Grafen/PEDOT: PSS dengan jumlah muatan pengisi 1.0vol% masing-masing menunjukkan 90% dan 81% peningkatan dalam kekonduksian elektrik dan haba berbanding dengan kompisit epoksi terisi grafen.

SYNTHESIS AND CHARACTERIZATION OF GRAPHENE FILLED EPOXY AND PEDOT:PSS COMPOSITES

ABSTRACT

The discovery of graphene composites has driven changes among researchers because of their unique properties. The aim of the present study is to synthesize graphene and used as a filler in epoxy composites. The performance of synthesize graphene in epoxy was compared with commercialize graphene. Graphene was synthesized using modified Hummer's method and spin coating was used to produce epoxy composites with varying amount of filler loading. Analysis from Raman spectrum of synthesize graphene showed an increase in intensity ratio (I_D/I_G) which indicates the decrease of average size of the sp^2 domains upon reduction of the GO. This is due to the loss of carbon formation. Besides that, FTIR spectra showed that the graphite has been successfully oxidized due to the presence of peak which referring to oxygen-containing groups. The best graphene filler loading in epoxy composites was obtained at 0.4vol% based on thermal conductivity measurement which indicate 37.5% increment compared to unfilled epoxy. Additionally, graphene/epoxy composites shows that the addition of filler in epoxy generally increase the electrical conductivity value from 7.38×10^{-6} to 7.19×10^{-5} S/cm, which is two order of magnitude higher than unfilled epoxy. Graphene/PEDOT:PSS with 1.0vol% loading exhibits 90% and 81% improvement in electrical and thermal conductivities, respectively compared to graphene/epoxy composite.

CHAPTER ONE
INTRODUCTION

1.1 Overview

The usage of graphene in recent years has received a significant attention from researchers due to their unique properties and numerous potential applications in various industries. This 2D nanomaterial is made up of a single or few-layers sheet of sp^2-hybridized carbon atoms that make it the nest and strongest material known (Khanam et al., 2015). In fact, there are many works have been done on the synthesis and characterization of graphene because of their flexibility. However, Du and Cheng (2012) reported that the synthesis method strongly affect the intrinsic properties of graphene.

The graphene synthesis can be classified into exfoliation (Tripathi et al., 2013), chemical vapor deposition (CVD) (Juang et al., 2010), Hummer's method (Shahriary and Athawale, 2014) and epitaxial growth on substrate (Sutter et al., 2008). Among these methods, the most promising method for large scale production of graphene is the Hummer's method or also known as reduction of graphene oxide (GO). Previous study by Guerrero and Caballero (2015) reported that in Hummer's method, GO consists of phenol hydroxyl and aromatic region of each sheet and sp^2- hybridized carbons containing carboxyl as well as carbonyl groups mostly at the edges and these groups offered huge chances for access to functionalized graphene based materials.

The oxidation of graphite to GO breaks up the sp^2-hybridized structure of stacked graphene sheets. Although GO can be readily dissolved in water and in organic

solvents after chemical modification, GO was found electrically insulating and thermally unstable (Carotenuto et al., 2012). Thus, in order to build up electrical conductivity, at least partial reduction of graphene oxide is required. A number of different methods currently exist for the reduction of GO to produce chemically modified graphene such as thermal reduction and chemical reduction (Pei and Cheng, 2011; Mahanta et al., 2015).

The increasing interest in composites polymer is accelerated by the development of graphene particles in recent times. These composite materials demonstrate significant change in properties that cannot be accomplished by utilizing virgin polymers. The extent of the improvement is related directly to the degree of dispersion of the fillers in the polymer matrix. Thereby, the unique properties of graphene polymer composites are derived from the amount of filler loadings in the polymer grid (Park and Seo, 2011).

Different types of graphene, such as expanded graphene and exfoliated graphene, have likewise been utilized to produce conducting composites with progressed physicochemical properties. There are many studies on expanded and exfoliated graphene composites based on a range of polymers, including epoxy (Ganguli et al., 2008), poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Liu et al., 2015), poly(methyl methacrylate) (PMMA) (Ramanathan et al., 2008), linear low-density polyethylene (LLDPE) and high-density polyethylene (HDPE) (Kim et al., 2009), polystyrene (Balamurugan & Berchmans, 2015) and polyaniline (Yan et al., 2010).

It was reported that epoxy resin is one of the most common type of thermosetting resin used in graphene composites (Wei et al., 2015). The advantage that epoxy can offer are in terms of its flexibility, low processing temperature and easily fabricated into various shape. However, epoxy resin showed very poor thermal conductivity but the inclusion of graphene sheets resulted in significant improvements (Kuilla et al., 2010). Besides that, as studied in Soltani et al (2015), PEDOT:PSS also has attracted much attention in conducting polymers family to incorporated with graphene fillers due to its excellent properties such as high electrical conductivity. The formation of 3D conducting networks in PEDOT chains leads to conductivity enhancement.

On the other hand, important areas of research in graphene based polymer composites have already been explored for a range of applications in different fields such as electronic devices (Eda et al., 2008), energy storage (Song et al., 2012), sensors (Xu et al., 2010) and biomedical applications (Chen et al., 2011). Due to the performance of graphene composites which are high electrical conductivity, high carrier mobility and moderately high optical transmittance in the visible range of spectrum, graphene based polymer composites have been used as electrodes for dye-sensitized solar cells, organic solar cells, liquid crystal devices, organic light emitting diodes and field emission devices (Hong et al., 2008; Wu et al., 2008). Transparent conducting films are used in many electronic devices as in solar cells, touch screens and flat panel display (Wang et al., 2012).

1.2 Problem Statements

After few years of discovery and development of graphene based composites, few progresses had been reported globally. Although the potential of graphene in variety applications had been determined, there are still some limitations that need to be conquered. The major challenge is to produce high quality graphene with selected number of layers even though diverse synthesis method for graphene had been studied. Most of the synthesis methods focused on the quality of graphene but ignore other important factors such as cost, environmental impact and processing method.

Previous researchers reported that modified Hummer's method is able to minimize the cost where the use of graphite flakes reduce the production cost of graphene (Wang et al., 2016). Although graphene can be derived more economically via modified Hummer's method, but it still have some limitations including production of acid wastes, the oxidation reaction involves potential risks for explosion, toxic gas generation residual and low yield (Mukhopadhyay and Gupta, 2012). Different types of oxidation agent will influence the generation of toxic gas. For example, $KClO_3$ was replaced by $KMnO_4$ as the oxidation agent, hence the toxic gas was removed and the securities of experiments were improved (Chen et al., 2013).

Besides that, the chemical reduction of graphene oxide (GO) typically involves highly toxic reducing agents that are harmful to human health and environment. Hence, in this study hydrazine was replaced by Zinc powder due to its nontoxic properties. The modified Hummer's method remains a key point of interest because it is an easy method of producing large quantities of graphene.

To date, many fabrication methods exist to incorporate fillers into the polymer matrices such as in-situ polymerization, melt intercalation, solution mixing and spin coating (Kuilla et al., 2010). In order to achieve optimal enhancement of graphene polymer composite, spin coating was used as fabrication method in this study since the solution can be easily dispersed on spin coat and the thickness of the film also can be control by changing the speed. Moreover, this method allows graphene to be mixed with matrices at low filler loading due to the limitation in viscosity, thus will reduce the nanoparticle agglomeration development. These fabrication methods of composites are important in determine the filler matrix adhesion that will affect the properties of the composites.

1.3 Objectives

The objectives of the present study are as follows:

1. To synthesize and characterize graphene produced via modified Hummer's method.
2. To investigate the effect of filler loadings and different types of graphene (synthesized and commercialized) filled epoxy composites on morphology, thermal and electrical conductivity.
3. To compare the effect of graphene filled epoxy and PEDOT:PSS on thermal and electrical conductivitiy of the polymer composites.

1.4 Thesis outline

There are five chapters in this thesis, which each chapter offers information related to the overall research study. Chapter 1 presents a brief introduction with the background, problem statement and objectives of this study. Chapter 2 consists of literature review on the synthesis method, fabrication method of graphene filled polymer film composites as well as a brief coverage of its characterizations. Next, chapter 3 provides the materials used in the experiment, followed by experimental procedure and characterization method. Chapter 4 can be divided into three parts. The first part discusses the characterization of graphene synthesized by Hummer's method. The second part explores the discussion on the comparison between synthesis graphene and commercializes graphene at different filler loading in epoxy system. Followed by third part which describes the properties of the graphene filled polymer composites by using different matrices. In addition, this chapter also includes the findings regarding the effect of graphene towards the electrical and thermal conductivity. Lastly, Chapter 5 gives the conclusion on the present investigation as well as some suggestions for further research.

CHAPTER TWO
LITERATURE REVIEW

2.1 Introduction

2.1.1 Background of graphene oxide

Oxidized graphite is practically referred to as graphene oxide (GO). The first reported synthesis of GO was by Brodie et al. in 1858. Hummers and Offeman in 1957 modified the procedure to make it safer. Up to today this synthetic procedure, which is now generally referred to as Hummers method, remains one of the primary ways of producing bulk GO, though there are other methods that have been also developed.

Graphene oxide, in its as prepared form, has a structure similar to graphene, except that most of the sp^2 hybridized carbon atoms become sp^3 hybridized due to the introduction of the oxygen containing functional groups. Though there are variations in the amounts and types of the functional groups introduced into graphene upon oxidation. Due to the polar nature of the attached functional groups, GO can form stable colloidal dispersions in water and other polar solvents. Because of the same functional groups, GO can be a wide-bandgap semiconductor or an insulator with a bandgap as large as ~4 eV, depending on the level of oxidation (Yan et al., 2009). Additionally, sheet resistance of GO is ~ 1010 Ω/sq (Gilje et al., 2010) compared to ~ 30 Ω/sq (Chen et al., 2008) for pristine graphene on SiO_2. Because of these inferior electrical conductivity values, oxygen containing functionalities have to be removed from GO, the process is termed graphene oxide reduction.

2.1.2 Background of reduced graphene oxide

Chemical reduction approaches are widely used for removing oxygen containing functionalities from graphene oxide (GO). Reduction with hydrazine hydrate ($NH_2NH_2 \bullet H_2O$) of GO solution (Stankovich et al., 2006) and with hydrazine vapor of GO thin films are most commonly used methods. One of the drawbacks of using hydrazine reduction method is the introduction of heteroatomic impurities, specifically in the form of covalently bound nitrogen species (e.g. hydrazones, amines, aziridines) which can act as n-type dopants (Shin et al., 2009). Reduction with sodium borohydride ($NaBH_4$) (Jeon et al., 2012) is advantageous over hydrazine approach, because no impurity incorporation occurs. However, the overall reduction efficiency with sodium borohydride is not as high as with hydrazine. Another approach that compete the hydrazine reduction method, yet lacks its drawbacks is based on treating GO films for 1 h at 100 °C in 55% is hydroiodic acid (HI) (Pei et al., 2010).

Other than chemical reduction, thermal reduction of GO is another widely used approach for RGO. Unlike chemical reduction, thermal reduction can be subdivided on bulk and nanoscale reduction. Bulk reduction is generally performed in vacuum (Ghosh et al., 2012) or in an inert environment (Schniepp et al., 2006) at temperatures as high as 1900 °C to achieve the best possible quality of the reduced material. Nanoscale reduction is performed with a heated atomic force microscope (AFM) tip at temperatures approaching ~1100 °C. Thermally reduced graphene oxides, depending on the reduction temperatures, vary in their final oxygen content and the sheet resistance values. Generally, GO films that are thermally reduced exhibit better characteristics then their chemically reduced counterparts (Wei et al., 2010). This is primarily due to a more complete removal of the oxygen containing functionalities.